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Thermal decomposition of asphaltenes

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The thermal decomposition of Athabasca asphaltene at relatively low ($<350^{\circ}\text{C}$) temperatures is believed to proceed by elimination of groups situated on peripheral sites of the asphaltene. More severe degradation of the asphaltene structure does not occur until elevated ($>350^{\circ}\text{C}$) temperatures are attained.

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Bitumens and petroleum are predominantly hydrocarbon in nature; they do, however, contain appreciable amounts of organic non-hydrocarbon constituents, mainly nitrogen-, oxygen- and sulphur-containing compounds. These constituents usually appear throughout the entire range of bitumen fractions but tend to concentrate mainly in the heavier fractions and in the non-volatile residues^{1,2}. Although their concentration in the various fractions may be quite small, their influence is nevertheless quite important. Of special importance is the asphaltene fraction in which the non-hydrocarbon constituents tend to concentrate³ and which appears to be responsible for a large proportion of the coke produced during a thermal operation. It was therefore of interest to expand the investigations described earlier on the thermal cracking of the Athabasca bitumen^{4,5}. The present communication describes the thermal treatment of the asphaltene fraction from Athabasca bitumen and attempts to determine the course of the thermal reaction by investigating the nature and production of the gaseous materials and the non-volatile residue.

EXPERIMENTAL

Weighted amounts of dried ($70^{\circ}\text{C}/2.7\text{ kPa}/50\text{ h}$) demineralized asphaltene (*ca.* 2.5 g), separated from Athabasca bitumen in the manner described elsewhere⁶, were placed in a silica tube, in a conventional tube furnace, flushed by a stream of dry nitrogen ($>99.9\%$ purity) raised to the designated temperature at $5^{\circ}\text{C min}^{-1}$ and maintained at that temperature for 1.5 h. The composition of the gaseous products was determined using a Fischer Gas Partitioner equipped with two columns - one 183 cm \times 6.4 mm (6 ft \times 1/4 in) packed with di-2-ethylhexyl-sebacate on 60-80 mesh Chromosorb P and the other 198.3 cm \times 9.5 mm packed with 40-60 mesh molecular sieve - maintained at 70°C using dry helium as the carrier (40 ml min^{-1}) gas. The proportions of propane and butane in the gaseous products were estimated by means of a gas chromatograph equipped with a silica-gel column (305 cm \times 9.5 mm) and a thermal-conductivity cell. Non-volatile products were con-

tinuously extracted (Soxhlet) with pentane and then with benzene until all extracts were colourless (*ca.* 24 h).

The experimental technique did not allow estimation of the sulphur dioxide which is known to be produced during the thermal decomposition of asphaltene⁷.

Elemental analyses were determined by the Alfred Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, West Germany.

RESULTS

The thermal decomposition of the asphaltene occurred readily at a variety of temperatures to yield products varying from low-molecular-weight gases on the one hand to presumably high-molecular-weight, benzene-insoluble material on the other.

The data presented in Table 1 show that gases are released from the asphaltene at low temperatures, and that there is a significant increase in the amounts of these products over the temperature range $200-600^{\circ}\text{C}$. The product distributions are markedly different at temperatures above 350°C . For example, the yields of the C_1-C_4 paraffins rise from 81.5 mmol/100 g asphaltene to 185.5 mmol/100 g asphaltene at 400°C . Similarly, at temperatures above 350°C , hydrogen sulphide is an important component of the gaseous products, there being only 5 mmol/100 g asphaltene at 300°C but rising to 24.5 mmol $\text{H}_2\text{S}/100\text{ g}$ asphaltene at 400°C . It is also significant that the gaseous products contain substantial proportions of the oxygen and sulphur originally present in the asphaltene (Table 2).

The evolution of gases (CH_4 , C_2H_6 , CO and CO_2) from the asphaltene at low ($<300^{\circ}\text{C}$) temperatures is at first surprising, but it is known that first condensed aromatics and then alkyl derivatives will produce hydrocarbon gases at moderate temperatures^{7,8} and the oxygen-containing gases could conceivably arise from the facile decomposition of the various oxygen functions that are reputed to be present in the asphaltene^{9,10}. Indeed, gases of this type have been shown to be present in the oil sand at formation tempera-

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Table 1 Gas distribution from asphaltene pyrolysis

Temperature (°C)	Fraction of asphaltene appearing as gases (wt %)	Volume of gases per 100 g asphaltene (cm ³)	Gas analysis (v/v %)									
			H ₂	CO ₂	CO	H ₂ S	CH ₄	C ₂ H ₆	C ₃ H ₈ + C ₄ H ₁₀	C ₂ H ₄ + C ₃ H ₆	CO	H ₂
200	1.7	760	0	47.8	0	0	26.8	25.4	0	0	16.0	0
250	2.5	1450	0	30.9	11.6	0	33.6	23.9	0	0	7.5	0
300	4.3	2750	0	17.5	11.8	0	39.7	24.9	0	0	14.5	0
350	8.5	5000	1.3	10.7	7.8	4.1	59.7	15.4	0.7	0.2	17.5	3.0
400	18.5	6000	4.7	8.7	6.9	8.1	53.0	13.4	2.8	0.4	18.5	12.5
450	40.4	8000	10.2	7.8	6.7	10.3	50.6	10.8	3.2	0.4	24.0	36.5
500	49.5	10000	9.3	7.8	5.4	9.4	51.5	12.3	3.8	0.5	24.0	41.5
600	54.3	12000	12.6	7.0	5.1	10.5	48.6	11.5	4.2	0.6	27.3	67.5

tures¹¹. The simultaneous generation of benzene-insoluble material (Table 3) indicates the presence of a thermal condensation reaction even at these low temperatures. The presence of higher paraffins (C₃H₈ and C₄H₁₀), the olefins (C₂H₄ and C₃H₆) and the remaining non-hydrocarbon gases (H₂ and H₂S) at elevated temperatures indicates the occurrence of a more severe thermal degradation. Indeed, it is significant that the generation of several of these gaseous materials is usually accompanied by an inflexion point in the range 350–450°C (Figures 1 and 2) suggesting that two thermal processes may be occurring. Presumably, at temperatures <350°C the more thermally labile groups, such as those on peripheral sites, are eliminated whilst at higher temperatures (>350°C) more severe degradation of the asphaltene molecule occurs.

The non-volatile products produced by thermal treatment of the asphaltenes can be conveniently divided into three fractions by solvent treatment (Table 3). It has been shown previously that thermal decomposition of the

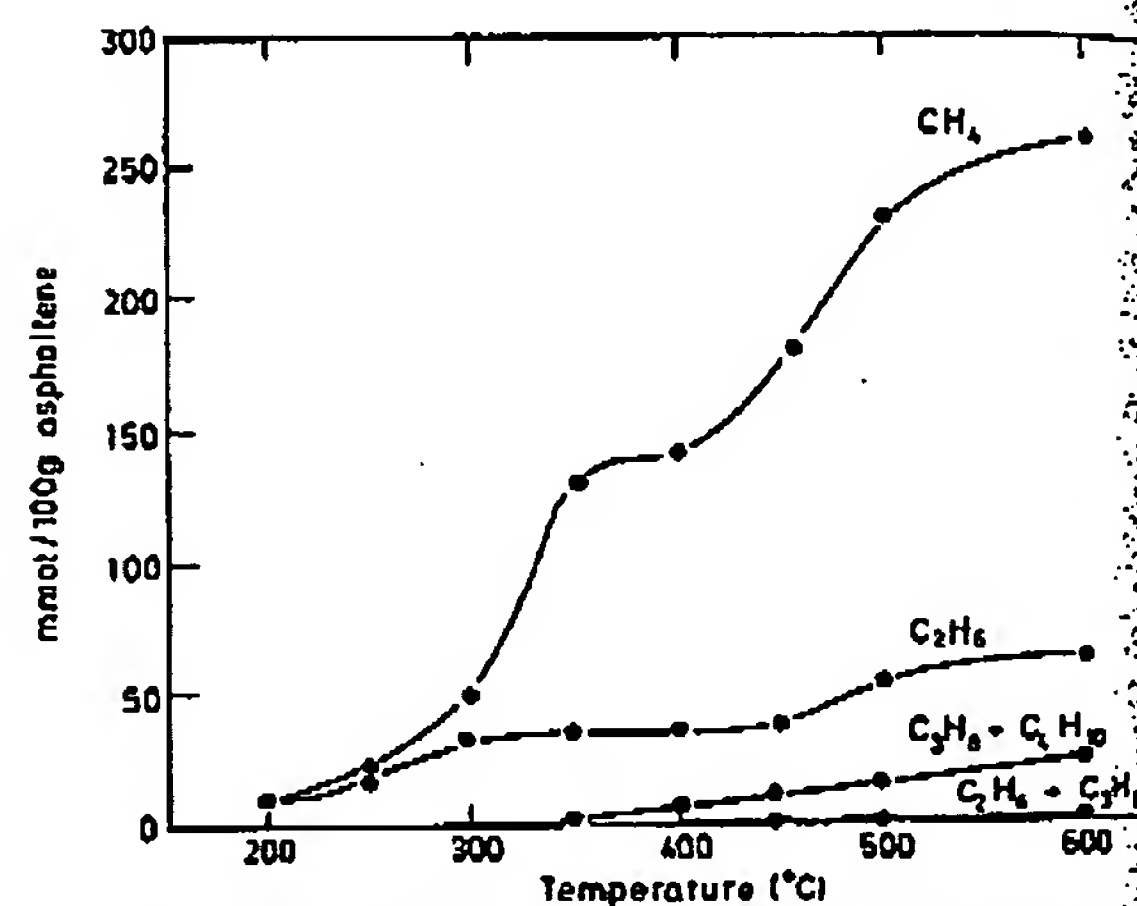


Figure 1 Hydrocarbons evolved during asphaltene pyrolysis

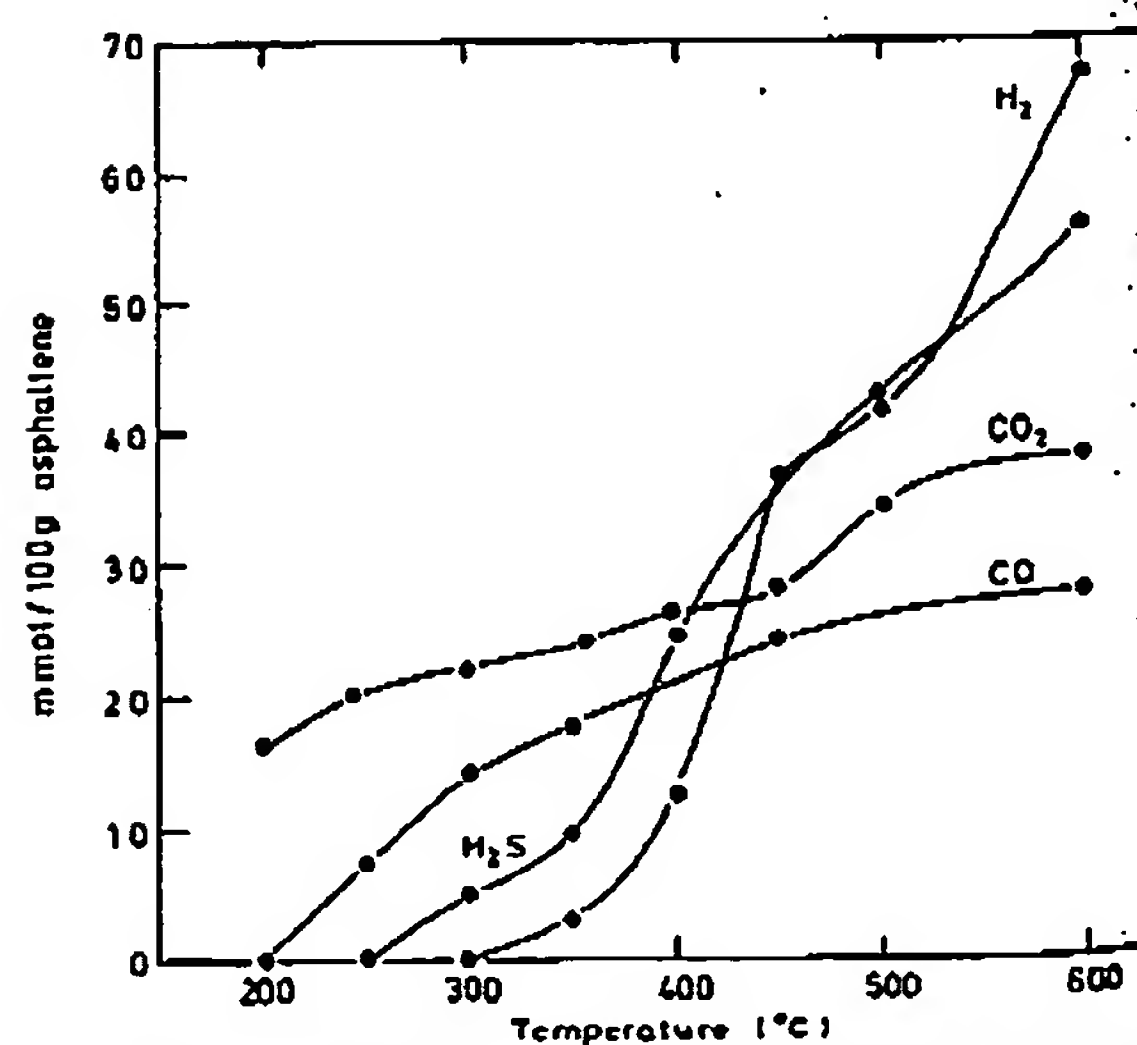


Figure 2 Non-hydrocarbons evolved during asphaltene pyrolysis

Table 2 Distribution of elements among gaseous products^a

Temperature of pyrolysis (°C)	% C appearing as total gases	% C appearing as hydrocarbons	% H appearing as H ₂	% O appearing as CO ₂ + CO	% S appearing as H ₂ S	% H appearing in total gases
Untreated	0.63	0.39	0	20.48	0	1.38
200	1.20	0.79	0	30.40	0	2.96
250	2.26	1.712	0	36.80	2.0	6.65
300	3.75	3.12	0.07	41.92	3.8	14.27
350	4.29	3.62	0.31	45.12	9.8	16.60
400	5.27	4.49	0.89	51.20	14.6	21.17
450	7.68	6.70	1.01	59.62	19.2	27.58
500	7.95	6.98	1.64	65.47	22.5	32.08

^a the weight of the element appearing in the gas expressed as a percentage of the element initially present in the asphaltene

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Table 3 Distribution of non-volatile products

Product data				
Temperature (°C)	% of original asphaltene	Fraction	% of product	Atomic H/C ratio
Untreated	100	Benzene soluble	100	1.237
200	98.3	Pentane soluble	4.5	1.368
		Benzene soluble	94.5	1.189
		Benzene insoluble	Trace	1.125
250	97.5	Pentane soluble	Trace	—
		Benzene soluble	95.0	1.194
		Benzene insoluble	4.5	1.115
300	95.7	Pentane soluble	Trace	—
		Benzene soluble	90.5	1.198
		Benzene insoluble	9.0	1.100
350	91.5	Pentane soluble	Trace	—
		Benzene soluble	81.8	1.112
		Benzene insoluble	18.0	0.995
400	81.5	Pentane soluble	Trace	—
		Benzene soluble	35.7	1.144
		Benzene insoluble	62.9	0.767
450	59.6	Pentane soluble	Trace	—
		Benzene soluble	21.4	1.156
		Benzene insoluble	78.2	0.582
500	50.5	Pentane soluble	0	—
		Benzene soluble	0	—
		Benzene insoluble	100	0.532
600	45.7	Pentane soluble	0	—
		Benzene soluble	0	—
		Benzene insoluble	100	0.448

asphaltenes will produce a fraction that can be removed by distillation⁴. Under the present experimental conditions it was not possible to isolate, or even produce, material of this nature, but some lower-molecular-weight material (pentane-soluble product) was generated in each experiment with the exception of the pyrolyses at 500°C and at 600°C.

The infrared spectra of the pentane-soluble products generally resemble those of the resins and oxidized resins^{11,12} having a broad absorption band at 3100–3500 cm⁻¹ (hydrogen-bonded hydroxyl), as well as bands at 1700 and 1720 cm⁻¹ (carbonyl functions), 1230 cm⁻¹ (carbon-

oxygen stretching), and bands at 1000 cm⁻¹, 1030 cm⁻¹, and 1100 cm⁻¹ (assigned to sulphur-oxygen functions). However, the spectra of these products showed definite decreases in the intensities of these bands with increase in temperature, indicating elimination of these oxygen-containing functions. Similarly, the infrared spectra of the benzene-soluble products generally resembled the spectra of the asphaltenes¹³, and, with the exception of the 1700 and 1720 cm⁻¹ absorption bands which were absent, contained similar bands in the 3100–3500 cm⁻¹ and 1000–1150 cm⁻¹ regions to those noted above; these also decreased in inten-

sity with an increase in temperature. Finally, the infrared spectra of the benzene-insoluble materials did not exhibit any of the aforementioned bands due to oxygen-containing functions but had absorption bands at 2920, 2850 and in the 1400–1500 cm^{-1} region (carbon–hydrogen) as well as a band at ca. 1600 cm^{-1} (carbon–carbon).

It is apparent from the aforementioned results that the thermal decomposition of Athabasca asphaltene occurs at relatively low temperatures – indeed, this may be strong evidence in favour of a low-temperature history of the bitumen. However, the measurable evolution of carbon dioxide (and ethane and methane) at 200°C could well arise from the presence of carboxylic functions (in the case of carbon dioxide) and thermally labile alkyl moieties (in the case of the hydrocarbon gases) on the periphery of the asphaltene molecule. The rapid increase in the evolution of the various gases at temperatures above 350°C is believed to be due to more severe degradation of the asphaltene.

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